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Lucia M. Petkovic
Daniel M. Ginosar
Harry W. Rollins
Kyle C. Burch
Patric J. Pinhero
Helen H. Farrell

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Lucia M. Petkovic*, Daniel M. Ginosar, Harry W. Rollins, Kyle C. Burch, Patrick J. Pinhero, and Helen H. Farrell

Idaho National Laboratory, Idaho Falls, ID, 83415-2208 (United States)

*Lucia.Petkovic@inl.gov

Introduction

Production of hydrogen by splitting of water at lower temperatures than by direct thermal decomposition can be achieved by a series of particular chemical reactions that establish a thermochemical cycle [1]. Among the high number of thermochemical water-splitting cycles proposed in the literature [2], the sulfur-based group is of considerable interest. All the sulfur-based cycles employ the catalytic decomposition of sulfuric acid into SO₂ and O₂. The produced O₂ corresponds to the O₂ generated from water in the overall cycle.

Research performed at the Idaho National Laboratory [3] has found that even one of the most stable catalysts, Pt supported on low surface area titania, deactivates with time on stream (TOS). To develop an understanding of the factors that cause catalyst deactivation, samples of 1% Pt supported on titania (rutile) catalyst were submitted to flowing concentrated sulfuric acid at 1123 K and atmospheric pressure for different TOSs between 0 and 548 h and a number of chemical and spectroscopic analyses applied to the spent samples.

Materials and Methods

Activity measurements were performed on a commercially-available 1% platinum supported on titania (rutile) catalyst (Johnson Matthey, West Deptford, NJ). The experimental setup consisted of a high-temperature, continuous-flow testing system built of Teflon tubing, glass, and quartz. The catalyst sample was loaded in a quartz tube reactor and reduced with hydrogen at 673 K for 2 h. The temperature was increased to 1123 K and then concentrated sulfuric acid was pumped into the system where the acid vaporized, thermally decomposed to SO₃ and H₂O, and the SO₃ reduced to SO₂ and O₂ over the catalyst bed. The unreacted SO₃ recombined with H₂O in the colder sections downstream of the reactor and was collected as a solution. The gaseous SO₂ and O₂ products were analyzed by gas chromatography. Once pre-selected TOSs (i.e., 24, 66, 102, and 548 h) had elapsed, the experiment was stopped and the spent catalyst recovered and submitted to post-operation analyses including scanning electron microscopy, elemental analysis, and diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS).

Results and Discussion

Catalyst activity declined about 46% over the 548 h of reaction testing as shown in Figure 1. The catalyst demonstrated an initial period of rapid deactivation until ca. 66 h TOS, a minor period of activity recovery from 66 to 102 h; and a region of moderate deactivation from 102 h through the end of the experiment at 548 h.

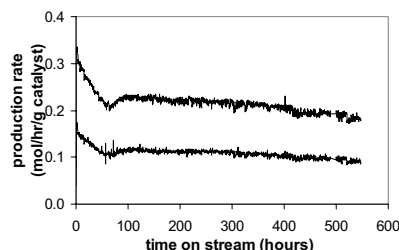


Figure 1. SO₂ (upper curve) and O₂ (lower curve) production rates as a function of TOS.

SEM analyses revealed an increase in Pt particle size with TOS. Some platinum volatilized and was found deposited on the inner reactor walls and also in the unreacted sulfuric acid collection. Sulfur species were found on the spent catalysts and DRIFTS analyses revealed that they were most likely bulk sulfates. However, the presence of sulfur species did not seem to correlate directly with catalyst deactivation. DRIFTS analyses of CO chemisorption showed the presence of oxidized platinum on the samples recovered at 24 and 66 h. The samples recovered at 102 and 548 h did not chemisorb CO. Density functional theory (DFT) modeling of sublimation and Ostwald ripening showed that the latter played an important role in catalyst deactivation.

Summarizing, the activity profile along with the results of post-operation analyses and DFT modeling suggested that a complex dynamic situation involving platinum sintering and oxidation, along with morphological changes of the support affected catalyst activity in a non-monotonic way.

Significance

Thermochemical water-splitting cycles consist of a series of chemical reactions to produce hydrogen from water at lower temperatures than by direct thermal decomposition. When the primary energy source to drive the cycle is nuclear or solar heat, hydrogen can be produced without the need of fossil fuels. The work reported in this contribution refers to the applicability of platinum supported on titania (rutile) catalysts for the sulfuric acid decomposition reaction, which is the common reaction in all sulfur-based thermochemical water-splitting cycles.

References

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